Quarterly Status Report
1 July 2007 to 30 September 2007
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Organization: University of Utah

Innovative Characterization of Amorphous and Thin-Film Silicon for Improved Module Performance

Research results during the first quarter of Phase III of NREL Subcontract XXL-5-44205-09 are reported. During this quarter we have finished our collaborations with United Solar Ovonics Corporation under this subcontract. Specifically, we have completed NMR measurements on another set of device-quality samples on which we have employed pulsed annealing to increase the defect densities. In addition, we are continuing our studies of light soaking at 77 K on two different samples to compare with the case of the tritium decay in the tritiated samples. These experiments will be completed in the next quarter. In this quarter we report on an update of our experiments of the production of silicon dangling bonds at 77 K in tritiated a-Si:H. In particular we discuss the annealing behavior.

The appearance of optically or electrically induced defects in hydrogenated amorphous silicon (a-Si: H), especially those that contribute to the Staebler-Wronski effect [1], has been the topic of numerous studies, yet the mechanism of defect creation and annealing is far from clarified. This quarterly status report describes our recent progress using another method to induce silicon dangling-bond defects by replacing some of the hydrogen, ^{1}H, with tritium, ^{3}H. Tritium decays to ^{3}He, emitting a beta particle (average energy of 5.7 keV) and an antineutrino. This reaction has a half –life of 12.5 years. The samples contain approximately 7 and 10.4 at.% tritium. In these tritium-doped a-Si: H samples each beta decay will create a defect by converting a tritium, which is bonded to silicon, to an interstitial helium, leaving behind a silicon dangling bond.

We have tracked these defects through electron spin resonance (ESR) and photothermal deflection spectroscopy (PDS) [2]. The densities we measured at room temperature were smaller by orders of magnitude than the number of tritium decays – only about $5x10^{17}cm^{-3}$. Therefore, there must exist a mechanism of defect annealing that is capable of healing ~ 10^{20} cm^{-3} defects at room temperature. In the present report, we extend these studies to 77K, in order to establish the thermal stability of the Si dangling bond defects introduced by tritium decay.

Both samples studied were made at the University of Toronto in 1996. The samples used in this experiment were deposited at glass substrate temperatures of 150ºC (further referred to as G181) and 225 ºC (referred to as G83). Shortly after deposition high temperature tritium effusion experiments determined the tritium concentration to be approximately 7 and 10 at. % in the two samples, respectively.

We expect the tritium decay to accumulate Si dangling bond defects because of the silicon-tritium bonds. The density of these defects is related to the number of tritium atoms that have decayed per unit volume. We first measured the samples 7 years after deposition, where the

density of tritium atoms that had decayed since making the films was about $6x10^{20}$ cm^{-3} [2]. However, both ESR and PDS measurements of the defect densities were lower by about 3 orders of magnitude because the defect density saturates at room temperature [2]. Next, we annealed the samples near the deposition temperature and kept the two samples at liquid nitrogen temperature for almost two years. During this time we used ESR to track the defect densities. After two years, the defect densities were about 10^{19} cm^{-3} for both samples. After two years in liquid nitrogen, we annealed the two samples. We step-wise annealed the G83 sample at successive temperatures up to 473 K isochronally while the G181 sample was annealed isothermally at 300 K.

After annealing the films, the defects began to accumulate in the dark at 77 K. The spin densities as functions of time stored at 77K are shown in Figs. 1 and 2 for the samples G181 and G83, respectively. The data at the shortest times are the defect densities just after annealing. These densities are about 10^{16} cm^{-3} and 10^{17} cm^{-3} for G181 and G83, respectively. In both cases, the densities are probably due to surface or interface defects. The spin densities increase linearly with time. The final data points are the defect densities after about two years. In Fig.1, the final density is about $3x10^{19}$ cm^{-3}, which is about 4 times lower than $1.4x10^{20}$ cm^{-3}, the density of tritium atoms, which have decayed since the sample was annealed. In Fig. 2, the final density is about $2x10^{19}$ cm^{-3}. In both samples there is no saturation in the growth in contrast to the case at 300 K. [2].

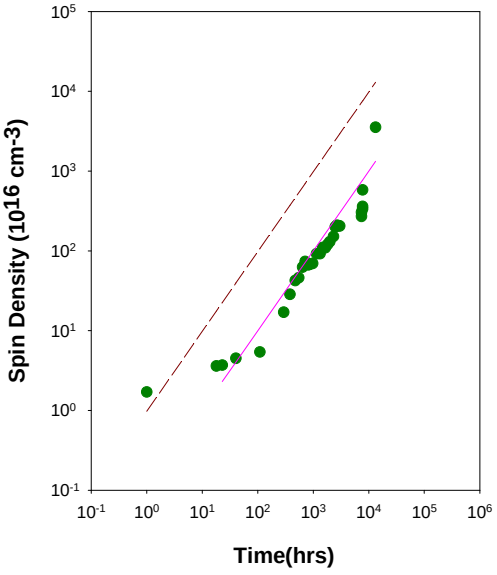

Figure 1. Increase of the defect densities of G181 as a function of time at 77 K.

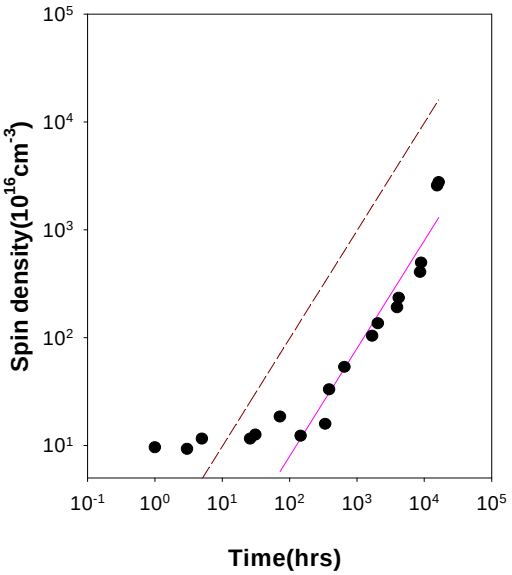

Figure 2. Increase of the defect density of G83 as a function of time at 77 K.

Figure 3 shows the decrease in defect densities after sample G181 was heated to room temperature and then kept at room temperature for several months. The defect densities were tracked by ESR. At 300 K the defects created at 77 K anneal slowly. Even after several months,

the density is still higher than the saturation density for defects created at room temperature, which is $6x10^{17}$ cm^{-3}. Only after about one year does the defect density reach the saturated value at 300 K[2]. Because PDS measures both charged and uncharged defects in the sample, we used this technique to check that the ESR was measuring all of the defects. The densities of defects, as measured by ESR in these samples of a-Si: H, are the same as those measured by PDS within a factor of two.

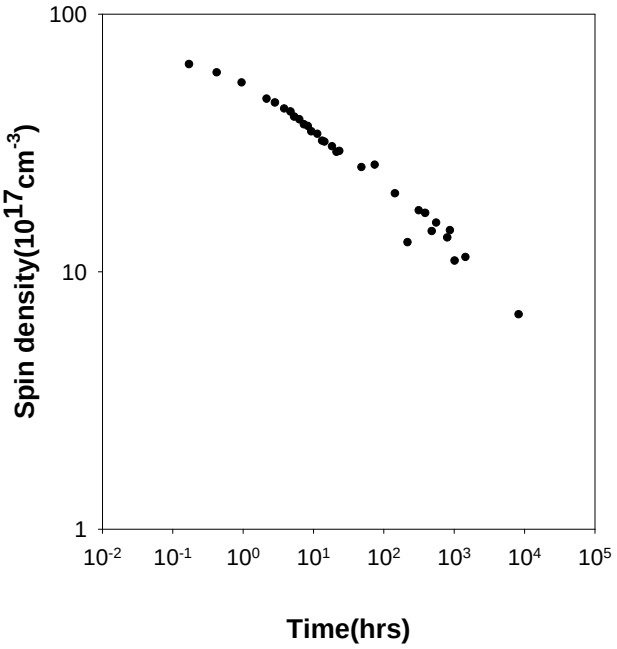

Figure 3. Decrease in the defect density after the sample G181 was heated to room temperature and then kept at room temperature for several months of isothermal annealing.

Figure 4 shows data for stepwise annealing of the G83 sample up to 380 K. The sample was kept for 30 minutes at each annealing temperature, T_a. We continued annealing step by step up to 380 K, and after each annealing step we measured the spin densities at 20 K. The data show that the defects are fully annealed at 473 K. The final density of approximately 10^{17} cm^{-3} matches the number after we annealed the sample at the start of the 77 K experiments.

At 77 K the defects accumulate almost linearly with the time. The spin density after two years is smaller than the density of tritium atoms that have decayed. This result possibly suggests that the tritium decay in a clustered hydrogen environment does not produce a dangling bond due to bond reconstruction as a result of emission of hydrogen from nearly Si atom. This suggestion is similar to the previous suggestion of thermal emission of hydrogen from the clustered phase [3, 7]. In addition, some tritium decays do not produce a silicon dangling bond because the tritium occurs in molecular form (trapped $^{1}H^{1}H$ or ^{3}H-^{3}H). The sample G83 was annealed step-by-step up to 200 ºC. Annealing results are similar to those that are observed when defects are created with light (Staebler-Wronski effect) at low temperatures. Two thirds of the

defects are annealed at around 300 K in our tritium sample. In some a-Si:H samples light soaked at 77 K essentially the same annealing kinetics is observed [4, 5].

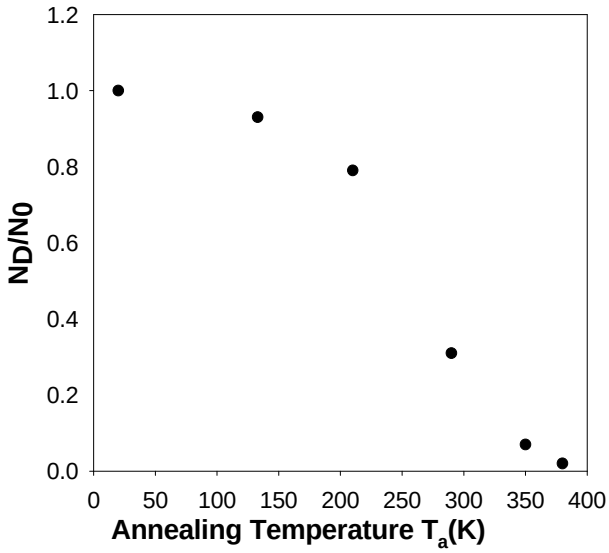

Figure 4. Relative decreases in defect density in sample G83 after stepwise annealing for 30 minutes at each successive annealing temperature, T_a.

In summary, we have shown that the defect densities of two tritiated amorphous silicon samples at 77 K increase linearly in time up to $10^{19}cm^{-3}$. The final densities, however, are factors of 4 to 8 smaller than the density of tritium atoms that have decayed. From NMR experiments, we know that 3 at. % of the atoms in the sample exists as hydrogen in the dilute phase and the rest is in the clustered phase [9]. Therefore, some of the clustered tritium atoms probably do not produce silicon dangling bonds at 77 K due to reconstruction. There is no evidence of saturation at 77 K. These results provide further hints for the role of hydrogen in creating defects in light soaked samples at low temperature as suggested in [6-8].

We expect to complete our collaborative studies with NREL on tritiated samples and samples light soaked at 77 K in the next quarter. Also, we will be initiating NMR studies of hot wire samples made with different nanocrystalline grain sixes in collaboration with Harv Mahan at NREL.

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